A Convenient Procedure for Hydrozirconation of Alkynes with i-BuZrCp$_2$Cl Generated in Situ by Treatment of Cp$_2$ZrCl$_2$ with t-BuMgCl

Douglas R. Swanson, Thinh Nguyen, Yumiki Noda,[1] and Ei-ichi Negishi*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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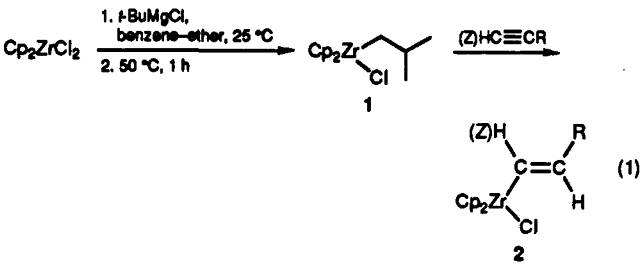
We have previously reported that the reaction of monosubstituted alkenes with 1.1 equiv of t-BuMgCl and 1 equiv of Cp$_2$ZrCl$_2$ in benzene–ether (5:1) at room temperature cleanly produces the corresponding monoalkylzirconium derivatives in high yields.[2] Unfortunately, our earlier attempts to hydrozirconate 1-octyne led to the formation of a mixture of 1-octene and n-octane after protonolysis.[3]

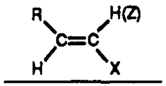
In our recent study requiring hydrozirconation of alkynes, we sought a convenient hydrozirconation procedure avoiding cumbersome filtration of soluble byproducts under an inert atmosphere required for the preparation of Cp$_2$Zr(H)Cl as a solid reagent.[4] We have found that treatment of 1-octyne with i-BuZrCp$_2$Cl (**1**), quantitatively preformed by treatment of Cp$_2$ZrCl$_2$ with 1 equiv of t-BuMgCl in ether at 25 °C and then at 50 °C for 1 h in benzene–ether (5:1), cleanly produces the desired (E)-1-octenylzirconocene chloride (**2a**) in 90% yield by ^{1}H NMR along with isobutylene (~100%). Protonolysis of **2** gave 1-octene in ≥95% yield along with only traces, if any, of n-octane and 1-octyne. Although the hydrozirconation reaction required ca. 48 h for ca. 90% completion at 25 °C, it was essentially complete in 5–6 h at 50 °C.



(1)

The experimental results are summarized in Table I. These results indicate that the scope of the current procedure appears to be comparable to those of the previously developed ones.[4] Thus, both terminal alkynes substituted with an alkyl or aryl group and internal alkynes, such as 4-octyne and 1-(trimethylsilyl)-1-octyne, react satisfactorily to give the corresponding alkenylzirconocene chlorides in high yields. Likewise, the current procedure is associated with the well-established high syn selectivity (>98%) of hydrozirconation, the high regioselectivity (>98%) observed with terminal and silylated alkynes, and the ability to accommodate certain heterofunctional groups such as Cl, SPh, and O(THP).[4d]

Table I. Hydrozirconation of Alkynes with i-BuZrCp$_2$Cl Generated in Situ by the Treatment of Cp$_2$ZrCl$_2$ with t-BuMgCl in Benzene at 50 °C

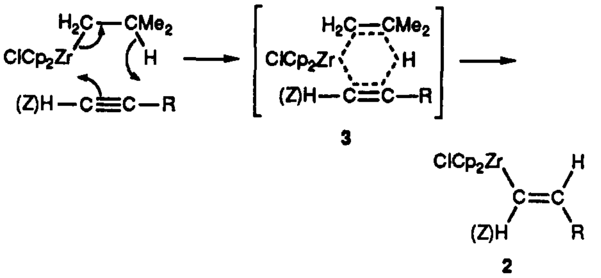
	hydrozirconation yield (%)			
alkyne	^{1}H NMR	GLC[a]	X	yield[b] (%)
n-HexC≡CH	95	91	D[7]	70
n-PrC≡CH	100	90[c]	I[11]	84
PhC≡CH	90	92	I[11]	68
n-PrC≡CPr-n	95	95	I[12]	80
n-HexC≡CSiMe$_3$	90	93	H[8]	75
Cl(CH$_2$)$_3$C≡CH		73	I[13]	68
PhS(CH$_2$)$_3$C≡CH	90	90	H[9]	80
THPO(CH$_2$)$_2$C≡CH	80	80	H[10]	77
$n\text{-Pent}\underset{\text{OSiMe}_2\text{Bu-}t}{\text{CH}}\text{C}\equiv\text{CH}$	90	90	I[14]	80

[a] GLC yield of the protonated product, unless otherwise mentioned. [b] Isolated yield. [c] GLC yield of (E)-1-iodo-1-hexene.

It appears important to complete the generation of **1** before addition of an alkyne to avoid side reactions such as that mentioned previously.[3] Some other organometals, such as t-BuLi and i-BuMgCl, may also be used to prepare **1**. However, t-BuMgCl is more economical than t-BuLi, and it leads to cleaner formation of **1** than i-BuMgCl. The use of i-BuLi[5] led to an extensive formation of (i-Bu)$_2$ZrCp$_2$.

Other chloroalkylzirconocenes, such as c-PentZrCp$_2$Cl, are also effective in hydrozirconating alkynes, but they have not displayed any advantages over i-BuZrCp$_2$Cl. The present procedure is remarkably insensitive to the nature of solvents. Thus, the reaction of 1-octyne with i-BuZrCp$_2$Cl has been satisfactorily carried out in THF, ether, benzene, and even hexane.

It is not clear at present whether or not **1** undergoes β-elimination to give first Cp$_2$Zr(H)Cl, which then reacts with an alkyne.[6] An alternate possibility is a concerted six-centered process via a transition state that may be represented by **3**.



(2)

Experimental Section

Manipulations involving organometallics were carried out under an atmosphere of N$_2$. Gas chromatographic measurements were performed on SE-30 (Chromosorb W) columns with appropriate hydrocarbon standards. THF and diethyl ether were distilled from sodium benzophenone ketyl; benzene and other hydrocarbons were distilled from LiAlH$_4$. Zirconocene dichloride was purchased from Boulder Scientific Co., and t-BuMgCl was purchased from Aldrich Chemical Co.

Hydrozirconation of 1-Octyne with i-BuZrCp$_2$Cl Generated in Situ. Representative Procedure. To Cp$_2$ZrCl$_2$ (5.84 g, 20 mmol) placed in a dry, nitrogen-flushed flask with a magnetic stirring bar, septum inlet, and an outlet connected to a mercury

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[1] On leave from UBE Industries, Japan.

[2] Negishi, E.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407.

[3] Although the reason for the observed complication is not clear, we may have prematurely added 1-octyne, which may have competitively generated 1-octynylmagnesium chloride.

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[6] Heating i-BuZrCp$_2$Cl at 50 °C for several hours does not give Cp$_2$Zr(H)Cl. This, however, does not rule out the formation of the latter as an intermediate.

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bubbler and covered with aluminum foil were added 40 mL of dry benzene and *t*-BuMgCl (2M, 10 mL, 20 mmol) in Et$_2$O. The reaction mixture was heated for 1 h at 50 °C to give a clear yellow solution. When the flask is not covered with aluminum foil, a brown mixture usually results. To the solution obtained previously was added 1-octyne (2.24 g, 20 mmol). The resulting mixture was heated for 6 h at 50 °C. Analysis of a small aliquot by ^{1}H NMR spectroscopy indicated that a singlet at δ 5.79 for the Cp group of *i*-BuZrCp$_2$Cl had cleanly shifted to δ 5.89 and that (*E*)-(1-octenyl)zirconocene chloride had been formed in 95% yield along with a nearly 100% yield of isobutylene (a multiplet at δ 4.75). After removal of the volatiles, the NMR spectra of (*E*)-(1-octenyl)zirconocene chloride were recorded with use of C$_6$D$_6$ as a solvent: ^{1}H NMR (C$_6$D$_6$, Me$_4$Si) δ 0.91 (t, J = 7 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.11 (q, J = 7 Hz, 2 H), 5.89 (s, 10 H), 6.87 (dt, J = 18 and 2 Hz, 1 H), (the signal for the α-alkenyl proton was not discernible); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ 14.40, 23.18, 29.59, 29.75, 32.31, 38.89, 113.15, 143.13, 176.38. These spectra indicated an isomeric purity of ≥98%. Analysis of a protonated aliquot by GLC also indicated the formation of 1-octene in 91% yield without the contamination by *n*-octane.

Another 5-mmol aliquot was evaporated, dissolved in 10 mL of Et$_2$O, and treated with D$_2$O at 0 °C. The resultant mixture was sequentially treated with 3 N HCl, extracted with Et$_2$O, washed with aqueous NaHCO$_3$, and dried over MgSO$_4$. Distillation gave 395 mg (70% yield) of (*E*)-1-deuterio-1-octene:[7] bp 112–114 °C; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.88 (t, J = 6 Hz, 3 H), 1.2–1.5 (m, 8 H), 2.04 (q, J = 7 Hz, 2 H), 4.98 (d, J = 17 Hz, 1 H), 5.81 (dt, J = 17 and 7 Hz, 1 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14.11, 22.66, 28.86, 28.95, 31.77, 33.80, 113.82 (t, J = 24 Hz), 139.15.

Hydrozirconation–Protonolysis of Alkynes. The following alkynes were converted to the corresponding alkenes following the representative procedure. **(a) 1-(Trimethylsilyl)-1-octyne.** The title compound (0.36 g, 2.0 mmol) was converted to 0.28 g (75%, 93% by GLC) of (*Z*)-1-(trimethylsilyl)-1-octene.[8] **(b) 4-(Pentynylthio)benzene.** The title compound (0.19 g, 1.0 mmol) gave 0.14 g (80%, 90% by GLC) of 4-(pentenylthio)benzene.[9] **(c) 2-(3-Butynoxy)tetrahydro-2*H*-pyran.** The title compound (0.15 g, 1.0 mmol) was converted to 0.12 g (77%, 80% by GLC) of 2-(3-butenoxy)tetrahydro-2*H*-pyran.[10]

Hydrozirconation–Iodinolysis of Alkynes. (a) 1-Hexyne. Representative Procedure. 1-Hexyne (0.17 g, 0.23 mL, 2.0 mmol) was hydrozirconated as described earlier. The reaction mixture was cooled to −30 °C, treated with iodine (0.76 g, 3 mmol) in 3 mL of THF, warmed to 25 °C, and quenched with 3 N HCl. Analysis by GLC indicated the formation of (*E*)-1-iodo-1-hexene in 90% yield. The mixture was extracted with pentane, washed with aqueous Na$_2$S$_2$O$_3$, NaHCO$_3$, and brine, dried over MgSO$_4$, and concentrated. Filtration through a silica gel pad (pentane) followed by evaporation afforded 0.35 g (84%) of (*E*)-1-iodo-1-hexene:[11] ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.89 (t, J = 7 Hz, 3 H), 1.2–1.5 (m, 4 H), 2.0–2.1 (m, 2 H), 5.97 (dt, J = 15 and 1.5 Hz, 1 H), 6.50 (dt, J = 15 and 7 Hz, 1 H); ^{13}C NMR (CDCl$_3$, Me$_4$) δ 13.98, 22.18, 30.70, 35.97, 74.63, 147.31. **(b) Phenylethyne.** The title compound (0.18 g, 1.8 mmol) was hydrozirconated in 90–92% yield. Iodinolysis with 0.63 g (2.5 mmol) of I$_2$ in 3 mL of THF afforded 0.28 (68%) of (*E*)-β-iodostyrene.[11] **(c) 4-Octyne.** The title compound (0.33 g, 3.0 mmol) was converted to 0.57 g (80%) of (*E*)-4-iodo-4-octene.[12] **(d) 5-Chloro-1-pentyne.** The title compound (0.10 g, 1 mmol) was converted to 0.16 g (68%) of (*E*)-5-chloro-1-iodo-1-pentene.[13] **(e) 3-(*tert*-Butyldimethylsiloxy)-1-octyne.** The title compound (0.72 g, 3.0 mmol) was converted to 0.88 g (80%) of (*E*)-3-(*tert*-butyldimethylsiloxy)-1-iodo-1-octene.[14]

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Supplementary Material Available: Experimental data for products formed (1 page). Ordering information is given on any current masthead page.

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Two New Abnormal Pathways in the Para-Claisen Rearrangement of 2-(Allyloxy)- and 2-(Crotyloxy)-3-hydroxybenzaldehyde†

S. Nicholas Kilényi,* Jean-Marie Mahaux, and Etienne Van Durme

Sanofi Research, 1, Avenue de Béjar, 1120 Bruxelles, Belgium

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As part of another project, we needed access to fairly large quantities of 5-allyl-2,3-dihydroxybenzaldehyde (**2a**). The obvious route to **2a** would involve the para-Claisen rearrangement[1] of the known compound 2-(allyloxy)-3-hydroxybenzaldehyde (**1a**). Compound **1a** was prepared as described[2,3] by regioselective alkylation of the monoanion of 2,3-dihydroxybenzaldehyde and thermolyzed neat at 160–170 °C. Unexpectedly, four products were obtained (Scheme I).

The major product, obtained in 50% yield, was indeed the desired 4-allyl isomer **2a**, accompanied by the expected decarbonylation product **5a**, and two other new compounds **3a** and **4a**. Insight into the nature of these rearrangements was obtained by repetition of the sequence with the crotyl analogue **1b**, which shows unequivocally that the reactions proceed exclusively by intramolecular concerted [3,3]-rearrangements.[4] There was no sign of allylic scrambling, which would be indicative of a fragmentation–recombination mechanism. The structures of **3a** and **4a** were confirmed by unambiguous synthesis (Scheme II). Thus, alkylation of the dianions of 3,4- and 2,3-dihydroxybenzaldehyde with allyl bromide takes place regiospecifically at the more basic meta phenoxide oxygen,[3] affording **6** and **7**, respectively. On thermolysis, an ordinary Claisen rearrangement to the vacant ortho position occurs, giving **3a** and **4a**. Interestingly, the temperature required to rearrange **6** was some 40 °C lower than that for isomer **7**.[5]

To the best of our knowledge, the meta-Claisen rearrangement of **1a,b** to **4a,b** is unprecedented. Neither can we find a precedent for the formation of **3a,b**.[6] These results are rationalized as shown in Scheme III.

We assume that the first [3,3]-sigmatropic shift occurs on the aldehyde side. The resulting cyclohexadienone intermediate has three possibilities: loss of CO giving **5**, [1,2]-shift of the formyl group to give the abnormal product **3**, or another [3,3]-shift. In the latter case, enolization gives the major product **2**. Alternatively, the allyl or crotyl group can undergo a [2,3]-shift, affording **4**.

Since, in this rationalization, **4** is derived by rearrangement of an enolizable cyclohexadienone, it should be possible to influence the product ratio by altering the rate of enolization. Schmid et al.[7] have shown that the further

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† For the sake of brevity "allyl" and "crotyl" are used throughout instead of "2-propenyl" and "(*E*)-2-butenyl".

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